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Spectral analysis of the chemical structure of carboxymethylated cellulose produced by green synthesis from coir fibre

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Abstract

In this work, CMC was synthesized from cellulose obtained from coir fibres. The obtained CMC yield was about 64.0 %. The Degree of Substitution value obtained was 0.44. The spectral pattern and thermogravimetric analysis of the synthesized CMC and cellulose were evaluated using FT-IR, XRD, and TGA/DTG. Characterization of the cellulose and CMC revealed their high crystallinity with cellulose showing a lower crystallinity value due to its lignin content. The CMC also showed a higher degree of crystallinity (56.93%) and hydrogen bonding compared to some earlier literature reports for CMC. The DTG curve revealed that the CMC had a maximum rate of degradation at about 310 ºC. The FT-IR spectra of the obtained CMC showed a finger print region characteristic of CMC (1590 cm^{-1}). This work shows that the spectral characteristic and crystallinity of CMC can be related to the synthetic method applied in obtaining the cellulose prior to CMC synthesis.

Keywords: carboxymethylcellulose; *spectral pattern; coir fibres; cellulose; liquid phase oxidation; degree of substitution.*

1. Introduction

Carboxymethyl cellulose (CMC) is a derivative of cellulose that seeks to functionalize cellulose so as to increase its application prospects [1-3]. Functionalization of cellulose by carboxymethylation has been exploited in applications such as drug delivery [4,5], polymer blending [6,7], tissue engineering [8,9], cation exchange resins [10], nanoparticles stabilization [11,12], mineral processing [13] among others [14-18]. To achieve these, etherification of the hydroxyl groups in the amorphous regions of cellulose with carboxymethyl groups was carried out. The etherification occurs mainly at the primary OH group on C(6) resulting in the reduction of the O6-H6...O3’ intra-chain hydrogen bonding interaction [19]. Depending on its degree of substitution (which corresponds to the average number of carboxymethyl groups per anhydroglucose unit), CMC shows variable solubility [2]. Previous studies on CMC was centered on the spectral elucidation, optimization of CMC yield under various reaction conditions, the improvement of its degree of substitution, as well as chemical modification of CMC structure [15,19-26]. Various structural elucidation tools have been used by researchers to evaluate the changes that occur during the carboxylmethylation of cellulose [2,19,27], these changes are dependent on several factors such as the method of isolating cellulose from the native fibre, degree of substitution and hence, purity [10,28].

Hydrogen bond energy (E_H) is an index that has been used in the study of hydrogen bonding in cellulose samples. The E_H offers a quantitative and simple method of comparing the degree of hydrogen bonding due to –OH groups in a cellulosic sample. To the best of our knowledge, there has been no reports on the use of E_H in the study and characterization of CMC.

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Earlier, Poletto et al. [29] reported on the structural differences in wood species using E_H, Li et al. [30] worked on hydrogen bonding in CMC using two-dimensional correlation infra-red spectroscopy. Nishiyama et al. [31] studied the crystal structure and hydrogen bonding network of cellulose using synchrotron X-ray and neutron fibre diffraction. Therefore, in this study a comparative spectral analysis of the synthesized CMC and cellulose obtained from coir fibre via a green synthetic method (hydrogen peroxide liquid phase oxidation of cellulose) was carried out and studied using FT-IR, XRD and TGA/DTG.

1.1. Structure

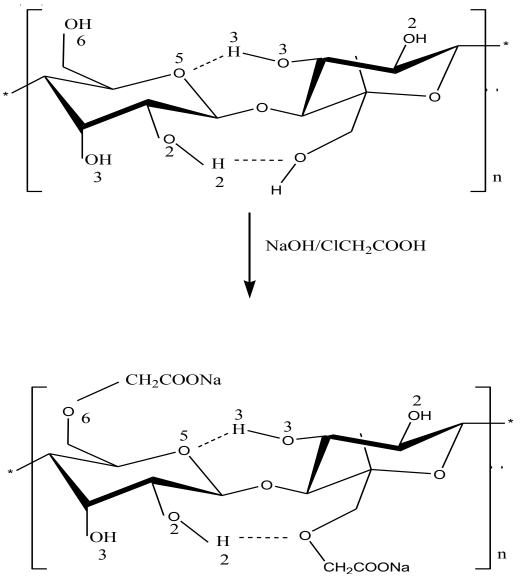

Fig. 1. Scheme showing hydrogen bonding (----) and carboxymethylation of cellulose.

Figure 1 shows a schematic representation of carboxymethylation process which proceeds via S_N2 mechanism. The amount of hydrogen bonding obtained in CMC as compared to ordinary native cellulose reduces due to the etherification of –OH group in native cellulose [2,32].

2. Experimental

2.1. Materials and sample preparation

Toluene, ethanol, acetone, hydrogen peroxide (50 %), isopropanol, NaOH (97 %), were purchased from Sigma Aldrich Inc. (USA), sodium monochloroacetate, methanol, acetic acid, nitric acid, HCl, phenolphthalein indicator were purchased from Merck AG Chemicals (Germany). All reagents were used as received. Type 1, Ultrapure deionized water (18.2 MΩ.cm, 25 ºC), Merck Millipore (Germany) was used for preparing all solutions. The coir fibres were obtained from dehusked coconut which was freshly harvested from a plantation in Benin-City, Edo-State, Nigeria.

2.2. Isolation of cellulose

The extraction of cellulose from coir was done using a two-step modified liquid phase oxidation method of Kazuhiro Mae et al. [33]. The pre-treatment step was done by placing 40 g of dewaxed coir fibres in an autoclave containing 400 mL of boiling de-ionized water. After 30 minutes of hot water treatment, the mixture was allowed to cool to 50 ºC, and the then transferred into cooling water to terminate the reaction. The pre-treated coir was washed with de-ionize water and ethanol till a clear filtrate was obtained, thereafter it was dried in a vacuum oven, re-pulverized and sieved to 250 µm mesh-size. The treated coir fibre was delignified liquid phase oxidation method. In a typical experiment, a ratio 1:10 mixture of the treated coir and 30% H_2O_2 was placed in a two-neck round bottomed flask under reflux for 12 h at 75 ºC. The oxidation reaction was terminated by adding excess cold water to the mixture. The mixture was then filtered, washed with de-ionized water and ethanol till a clear filtrate, was obtained, thereafter the obtained cellulose was dried in a vacuum oven at 60 ºC. The percentage yield of the cellulose was determined.

2.3. Synthesis of CMC

CMC from Coconut fibre was synthesized according to the procedure described by Bono et al. [34]. In a typical experiment, 5g of the isolated cellulose was placed in a flask, and 100 mL of Isopropanol was added with continuous stirring. Thereafter, 20 mL of 17.5% aqueous sodium hydroxide was added drop-wise into the mixture with continuous stirring for 1hr at ambient temperature. The reaction mixture was etherified by adding 6g of Sodium monochloroacetate (SMCA) at 50 ºC and stirred for 2hrs. The mixture (slurry) obtained was soaked in 200 mL methanol overnight. Neutralization of the obtained slurry with 90% of acetic acid was done till a pH of 7 was reached. The mixture was then filtered, purified by washing with 70% ethanol till a clear filtrate was obtained. The obtained CMC was dried in a vacuum at 60 ºC to constant weight prior to storage.

2.4. Determination of degree of substitution (DS) value

The DS value was determined using standard method ASTM D1439 [35]. 4g of the CMC sample and 75 mL of 95 % ethanol was agitated in 250 mL beaker for 5 mins. 5 mL of nitric acid was then added to the mixture, boiled, and stirred for 10 minutes. The resulting mixture was decanted and the sediment washed five times with 80% ethanol at 60 ºC, and thereafter with anhydrous methanol and then filtered. The obtained residue was dried at 105 ºC for 3 hours and cooled in a desiccator for 30 minutes. 0.5 g of dried acid-CMC was weighed into a 250 mL beaker, 100 mL of deionized water was added to the mixture while stirring. Thereafter, 25 mL of 0.3M NaOH was added to the mixture and was allowed to boil for 15 minutes. The mixture was titrated against 0.3M HCl using phenolphthalein as indicator.

The degree of substitution, was obtained using equations (1) and (2) below:

$$Carboxymethyl\ Content\,(\%CM) = ([Vo - Vn]M \times (0.059 \times 100))/m \quad (1)$$

$$Degree\ of\ substitution\ (DS) = (162 \times \%CM)/(5900 - (58 \times \%CM)) \quad (2)$$

Where:
Vo = Volume (mL) of HCl used to titrate the blank
Vn = Volume (mL) of HCl used to titrate sample
M = Molar concentration of HCl used
m = Amount of sample.

The molar mass of the anhydroglucopyranose unit (AGU) is 162 g/mol, and the molar mass of $-CH_2COOH$ group is 59 g/mol [36].

2.4.1. *Percentage yield calculation.*

The % Yield of Cellulose and CMC were determined using the formula below:

$$\%\ Yield\ of\ Cellulose = \frac{Mass\ of\ Cellulose\ obtained}{Mass\ of\ coir\ fibre\ used} \times 100$$

$$\%\ Yield\ of\ CMC = \frac{Mass\ of\ \ dried\ CMC\ obtained}{Dry\ Mass\ of\ Cellulose} \times 100$$

2.5. Characterization

The samples (CMC and cellulose) were dispersed in KBr matrix and compressed to form pellets. The FT IR spectra were recorded on these films using a Perkin-Elmer spectrophotometer in transmission mode. A resolution of 4 cm^{-1} was used and 64 scans were performed for each spectrum, in the range of 4000 cm^{-1} to 500 cm^{-1}. Powder X-ray diffraction studies were performed to determine the crystal structure of the CMC, Cellulose and Coir in a sample range of 5 -70º on an X-ray diffractometer (Philip's X'pert Pro) with Cu Kα radiation (λ = 0.154) employing an X'celerator detector and a monochromator at the diffraction beam side. Powder samples were used by employing a standard sample holder. The crystallinity index (CI) was calculated using the intensity values of the diffraction peaks corresponding to the crystalline and amorphous regions, according to equation 3 [37],

$$CI = \frac{I_{(002)} - I_{(am)}}{I_{(002)}} X100 \quad (3)$$

where $I_{(002)}$ is the counter reading at peak intensity of 2θ angle close to 22.6º representing crystalline material and $I_{(am)}$ is the counter reading at peak intensity of 2θ angle close to 18º representing amorphous material in coir cellulosic fibre. Thermal Gravimetric Analysis (TGA) of the CMC powder, cellulose and coir fibres were carried out on a TA Q50 series instrument in a platinum heating grid under a nitrogen flow rate of 30.0mL/min, at a heating rate of 10 ºC/min, and heated to 700 ºC using 10.76 mg of sample. TA-universal analysis 2000 software was used to extrapolate the Differential thermal analysis (DTA) curve.

3. Results and discussion

The yield of cellulose from coir was about 20.1 % as shown in Table 1. The low yield may be attributed to the loss of cellulosic materials during the isolation of cellulose from the fibres particularly at washing stage as well as the non-selectivity of hydrogen peroxide in oxidation reactions [37] which could have led to the degradation of the obtained cellulose. The degree of substitution value of 0.44 was obtained for the synthesized CMC. This low DS value is close to that reported for water hyacinth, Cavendish banana pseudo stem, sago waste, and sugar beet pulp cellulose [22,38-40] and may be the reason why the synthesized CMC was only slightly water soluble. Similar reports were obtained by Barai et al. [38].

Table 1. DS Value and % yield of CMC and cellulose.

Parameter	% Yield of cellulose	% Yield of CMC	DS value
Value	20.1±0.2%	64.00±0.04%	0.44

The FT-IR spectra of cellulose can broadly be categorized into the region corresponding to O-H and C-H stretching vibrations (3600 cm^{-1} – 2700 cm^{-1}) and the 'finger print region' (1800-1600 cm^{-1}) which is typical of the stretching vibrations and bending vibrations of various components of lignocellulosic fibres. The FT-IR spectra obtained for both the CMC and cellulose samples showed characteristic peaks at 3301 cm^{-1} and 3323 cm^{-1} respectively corresponding to O-H stretching vibrations. Peaks at 2879 cm^{-1} and 2885 cm^{-1} are characteristic of C-H stretching vibrations in the methyl and methylene groups in CMC and cellulose respectively. Peaks corresponding to carboxymethylation have been reported in the region 1500-1700 cm^{-1} .The band at 1587 cm^{-1} in the CMC spectra can be assigned to –COO stretching vibrations due to carboxymethylation of cellulose, the broader nature of this band in the CMC sample compared to the cellulose sample also confirms the carboxymethylation of the cellulose. The peak at 1507 cm^{-1} in cellulose can be assigned to C=C stretching of the aromatic ring in lignin. The presence of peaks at 1266 cm^{-1} in the spectra of cellulose can be assigned to guaiacyl/syringyl ring vibrations of residual lignin component in cellulose [10,27,28,41-45], indicating the presence of residual lignin in the isolated cellulose fibres. The near absence of this band in the CMC sample could mean that during the carboxymethylation process, a major part of the residual lignin in the cellulose was removed. The band at 1728cm^{-1} in the cellulose sample corresponds to the C=O stretching vibrations of carboxyl and acetyl groups of hemicellulose. Also the absence of this band in the CMC sample is indicative of the removal of hemicellulose during the carboxymethylation of cellulose. If this is the case, then a higher degree of crystallinity may be expected from the CMC compared to the cellulose, since lignin and hemicellulose in wood fibres is known to contribute to its amorphousity [1,29,46]. Lignin and hemicellulose have been reported to be lost during carboxymethylation of cellulosic samples [47]. The band at about 1025 cm^{-1} in the spectra of CMC and cellulose, can be assigned to C-H and C-O deformation in various groups in carbohydrates. Peaks at 1156 cm^{-1} in the spectra of CMC and cellulose correspond to C-O-C stretching vibrations while that at 660 cm^{-1} is assigned to C-OH out-of-plane bending in cellulosic samples [27,28,41,42,48].

The unique properties associated with cellulose are closely related to its hydrogen bonding network. The extent of hydrogen bonding in cellulosic materials can be readily estimated by the energy of hydrogen bonding obtained from the analysis of the FT-IR spectra. The method is based on the fact that hydrogen bonding results in a shift in the observed frequency for the O-H stretching vibration compared to that for free hydroxyl groups [43,46].

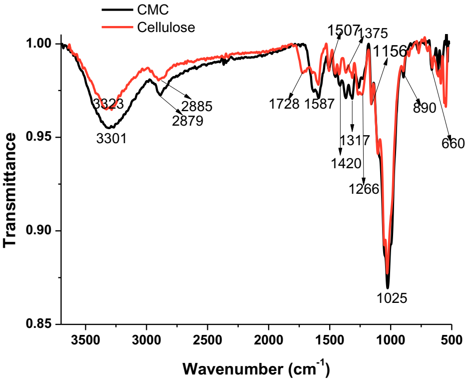

Fig. 2. FTIR spectra for CMC and cellulose.

The energy of hydrogen bonds (E_H) for CMC and cellulose was estimated using the equation [43],

$$E_H = 1/k[(v_o - v)/ v_o] \qquad (4)$$

where v_o is the frequency assigned to free hydroxyl groups (3650 cm^{-1}), v is the observed frequency for the hydrogen bonded hydroxyl groups and k denotes a constant ($1/k = 2.625 \times 10^2$ kJ).

The hydrogen bond distance (R) was estimated using the Pimentel and Sederholm equation [43],

$$\Delta v(cm^{-1}) = 4430 \times (2.84-R) \qquad (5)$$

where $\Delta v(cm^{-1})$ = (v_o -v) v_o is the monomeric OH stretching frequency with a value of 3600 cm^{-1} and v is the observed frequency in the IR spectra.

The E_H value obtained for cellulose was slightly lower than that for CMC as shown in Table 2. This implies that the degree of hydrogen bonding in cellulose was slightly lower than that in CMC. Considering the fact that carboxymethylation reduces the amount of available –OH groups for hydrogen bond formation [19], CMC would have been expected to have a lower degree of hydrogen bonding compared to cellulose. However, Li et al. [19] also pointed out the fact that the hydrophilic nature of the –COO group could also contribute significantly to hydrogen bond formation between water molecules and available –COONa and –OH groups. Also, high crystallinity has been reported to promote hydrogen bonding interactions in cellulosic materials [49].

Table 2. Parameters from FT-IR analysis of cellulose (a) and CMC (b).

FT-IR Indices	E_H (kJ)	R(Å)	IR Crystallinity Ratio		
			LOI H1420/ H890	TCI H1375/H2885	HBI A3323/A1317
(a)	23.52	2.78	1.13	0.77	2.02
(b)	25.10	2.77	1.19	1.08	1.54

Hence, considering the contribution of bound water and crystallinity to the degree of hydrogen bonding in cellulosic materials, the higher E_H value for CMC may be attributed to the higher degree of crystallinity in CMC (as revealed by XRD characterization in this study, Table 3) and the greater contribution of bound water (as revealed by the TGA plot in this study) to hydrogen bonding in CMC compared to cellulose.

The obtained CMC showed a much lower frequency of –OH absorption compared to previously reported studies by other researchers for both synthesized CMC and commercially available CMC with absorption frequencies of 3412.79 cm^{-1} (E_H = 17.06 kJ) and 3443.72 cm^{-1} (E_H = 14.84 kJ) for synthesized CMC and 3587.18 cm^{-1} (E_H = 4.52 kJ) for CMC obtained commercially [10]. Similarly, Li et al. [30] and Wang [14] reported on commercially available CMC of high absorption frequency for –OH stretching as compared to the our coir fibre synthesized CMC with an –OH stretching vibration reported at about 3530 cm^{-1} (E_H = 8.63 kJ) and 3443 cm^{-1} (14.89 kJ) respectively. This implies a much higher degree of hydrogen bonding in the obtained CMC compared to that in literature reports for synthesized CMC and the commercially available CMC. The absorption frequency for –OH stretching vibrations in CMC could be related to a number of factors including degree of substitution, amount of bound water, purity of sample, the temperature at which the –OH vibration was observed as well as whether the interaction is due to intermolecular or intramolecular hydrogen bonding [10,30].

The E_H values obtained for CMC and coir was higher than the reported values for Eucalyptus wood chips (16.23 kJ) but the R value obtained was close to that reported for Eucalyptus wood (2.80 Å) [44].

The crystalline nature of the CMC and cellulose samples were also characterized by FT-IR analysis following the method of Nelson and O'Connor [41,48,49]. The LOI (Lateral Order Index), TCI (Total Crystallinity Index), and the HBI (Hydrogen Bond Intensity) values were determined as shown in Table 2 above. The band at about 1420-1430 cm^{-1} was assigned by Nelson and O'Connor to the crystalline region of cellulosic materials while that at about 898 $cm^{-1}$was assigned to the amorphous region. The ratio of these bands was referred to as the LOI value and corresponds to the relative amount of crystalline and amorphous regions in the cellulose chains. TCI is a measure of the infra-red crystallinity index and was assigned as the ratio of the bands at about 1372 cm^{-1} and 2900 cm^{-1}. The degree of chain regularity, crystallinity and the extent to which water molecules are bound to the cellulose chains can be inferred from the HBI value. The HBI value is dependent on the mobility of the cellulose chains as well as their bond distance, and it is assigned to the ratio between the bands at about 3400 cm^{-1} and 1320 cm^{-1}. CMC had higher LOI and TCI values compared to cellulose. This may be attributed to the removal of residual lignin and hemicellulose from the cellulose sample during the carboxymethylation process. The TCI values obtained for CMC and cellulose were higher than values reported for *Pinus elliottii (0.474kJ)*, *Eucalyptus grandis (0.608kJ)*, *Mezilaurus itauba (0.237)*, and *Dipteryx odorata (0.389)* while the LOI values for CMC and cellulose was lower than that reported for the same fibres [50].

However, the use of LOI and TCI values in evaluating crystallinity of cellulosic samples has been reported as a very simplistic method which gives only relative values, this is because the assigned spectral bands usually contain contributions from both amorphous and crystalline regions [28,49].

The crystallinity of the synthesized CMC and cellulose were studied using XRD. The XRD peaks were assigned to the diffractograms (Figure 3) according to the native cellulose structure as described by Wada et al. [51]. The diffractograms for cellulose, CMC and coir showed characteristic peaks at 2θ angles of about 14.6-14.8º, 16.6-16.8º, 22.2-22.4º corresponding to the $(1\bar{1}0)$ crystallographic plane, (110) crystallographic plane, and (200) crystallographic plane respectively. The 2θ reflection at about 18.0-18.2º corresponds to the amorphous region of the cellulose. The CI values obtained for coir, cellulose and CMC were 38.40%, 38.75%, and 56.93% respectively. The higher degree of crystallinity in CMC compared to cellulose was contrary to earlier reports on CMC obtained directly from pure native cellulose, although, in the reported cases, the crystallinity of CMC varied with the degree of substitution. The higher degree of crystallinity in the obtained CMC compared to the synthesized cellulose can be ascribed to the low DS obtained for CMC, the higher degree of hydrogen bonding in CMC as well as the suspected removal of the residual lignin and hemicellulose (initially present in the synthesized cellulose) from CMC [10] and this was confirmed by FTIR analysis. This trend is in agreement with previous studies which showed that crystallinity increased as DS values reduced [27,38] and with loss of lignin and hemicellulose. [29,46,47]. The CI value for CMC obtained from waste paper [10] was lower compared to that obtained for our synthesized CMC. This is expected considering the degree of hydrogen bonding in the obtained CMC compared to that from the waste paper reported by Mohkami et al. (as pointed out in the FT-IR analysis). A number of literature reports have related the degree of crystallinity to the DS value of CMC [39,52], however, the pH of the process also affects the CI. This is evident in the work of Mohkami et al. [10] in which the CMC obtained from waste paper showed different CI values depending on the pH with the CMC in the alkaline medium showing a higher CI value of 27 (and higher degree of hydrogen bonding) compared to the CMC from neutral medium with a CI value of 21.

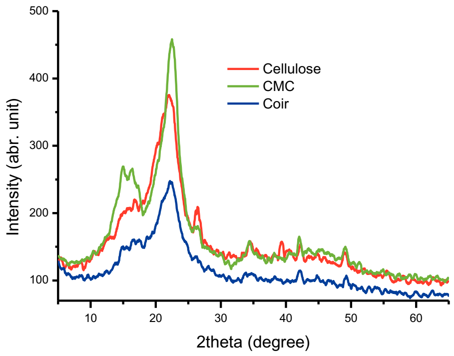

Fig. 3. XRD diffractogram of coir, CMC and cellulose.

Table 3. Parameters from XRD analysis of coir, CMC and cellulose.

XRD Parameter	Coir	CMC	Cellulose
CI%	38.40	56.93	38.75

The crystallinity index obtained from XRD characterization, agreed with the LOI and TCI values obtained for FT-IR analysis.

The thermograms from the TGA characterization of CMC and cellulose are shown in Figure 4. The plots show that CMC, cellulose and coir showed a weight loss of 8.66%, 8.26% and 8.60% respectively at about 100 ºC corresponding to the loss of water. The loss of water from CMC was higher than that reported (7.5%) by Li et al. [19].

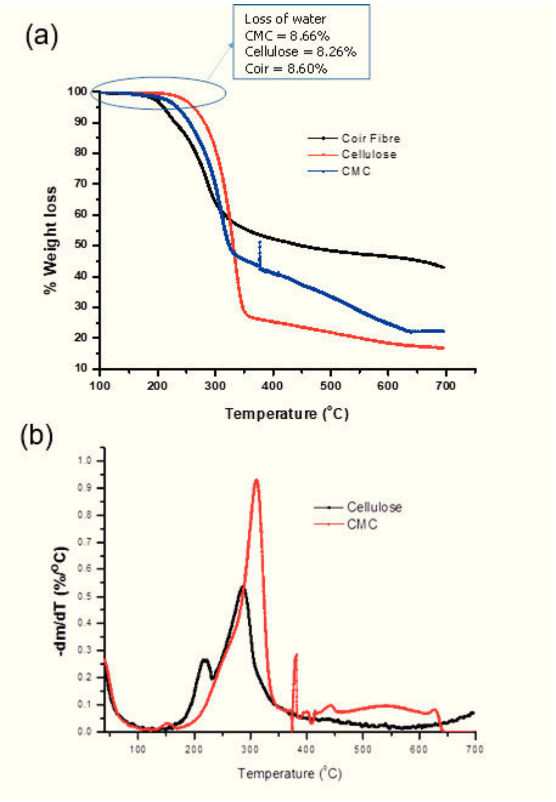

Fig. 4. TGA Thermograms (a) and DTG thermograms (b) for CMC and cellulose.

The presence of a significant amount of water in CMC, its higher degree of crystallinity, coupled with the hydrophilicity of the –COO group and its hydrogen bonding ability may have contributed to the high E_H value reported for CMC [19,27]. The decomposition of cellulose with increase in temperature followed a two-step process as expected for lignocellulosic materials. Generally, hemicellulose depolymerizes between 180 ºC and 350 ºC, and the glycosidic bonds cleave in random fashion between 275 ºC and 350 ºC. The decomposition of lignin occurs between 250 ºC and 500 ºC resulting in various products of pyrolytic decomposition (such as phenolics, hydroxyphenolics, guaiacyl-/syringyl-compounds) [45,46,50,53]. The peak in the DTG curve at about 230 ºC for cellulose corresponds to the region of maximum degradation of hemicellulose [46,50]. Instead of a peak, the DTG curve of the CMC sample only shows a shoulder in this region, this might be due to the loss of hemicellulose during the carboxymethylation of the obtained cellulose as predicted by FT-IR analysis. The peaks at about 290 ºC and 310 ºC for cellulose and CMC respectively is indicative of the inflection point (maximum degradation rate) for lignocellulosic samples and corresponds to degradation and depolymerization of various components of lignin and cellulose [45,46,50]. The percentage mass loss in the temperature range of 250-500 ºC was 75.12 % and 58.12 % for cellulose and CMC respectively. The lower weight loss occurring in CMC in this temperature range may be related to the lower content of lignin in CMC due to the loss of lignin in the carboxymethylation of cellulose, as initially indicated by FT-IR analysis.

4. Conclusions

CMC has been synthesized from coir via an environmentally friendly approach using liquid phase oxidation. The obtained CMC showed the presence of some spectral regions that are usually absent in pure CMC samples. This was attributed to the chosen method of synthesizing CMC applied in this study. The synthesized CMC showed average crystallinity and good thermal properties. However, due to its DS value (0.44), it was only slightly soluble in water.

Acknowledgements

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